

VII.F.4 Development of a 50kW Fuel Processor for Stationary Fuel Cell Applications Using Revolutionary Materials for Absorption-Enhanced Natural Gas Reforming

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Subcontractor:

Cabot Superior Micropowders, Albuquerque, NM

Contract Number: DE-FC36-03GO13102

Start Date: October 1, 2003

Projected End Date: September 30, 2006

Objectives

- Demonstrate a 50 kW absorption-enhanced reformer (AER) capable of providing near pure H₂ that meets DOE targets for efficiency and H₂ cost
- Develop high capacity, durable CO₂ sorbents and process to produce these sorbents in commercial quantities
- Test sorbents and optimize process using microreactors and 1kW scale reactors

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells, and Infrastructure Technologies Program Multi-year Research, Development and Demonstration Plan:

- A. Fuel Processor Capital Costs
- C. Operation and Maintenance (O&M)

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells, and Infrastructure Technologies Program Multi-year Research, Development and Demonstration Plan:

- A. Durability
- B. Cost
- I. Hydrogen Purification/Carbon Monoxide Cleanup

Technical Targets for Stationary Fuel Cell Fuel Processors

Target	Units	2005 Goal	Project Status
Cost	\$/kW	500	?*A
Cold Start-up	Minutes	<60	<20 on small scale
Transient Response	Minutes	<4	*B
Durability	Hours	>20,000	>1,000 hours demonstrated *C
Survivability	°C	-25 to 40	*B
CO Content	ppmv	5	<2
H ₂ S Content	ppbv (dry)	<5	< 20 ppb detection limit
NH ₃ Content	ppm	<0.1	<1 ppm detection limit

*A We do not have final cost estimates for reformer

*B Will not be measured until 50 kW reformer is built

*C Longer term tests will not be made until 50 kW reformer is built

Approach

- Develop calcium-based sorbents, reforming catalysts and water-gas-shift catalysts capable of shifting the natural gas/steam reforming equilibrium (in the temperature range of 550°C to 650°C) toward increased hydrogen concentration while capturing the carbon as calcium carbonate that is periodically regenerated to release carbon dioxide.
- Develop a process to convert sorbent powders into extrudates capable of undergoing many thousands of reforming/regeneration cycles without significant decrepitation.
- Optimize the absorption enhanced reforming process to produce near-pure hydrogen with greater than 78% thermal efficiency (lower heating value) using 1 kW reactors and dynamic simulation.
- Design, build, and operate a 50 kW natural gas reformer that meets DOE efficiency and cost targets.

Accomplishments

- Demonstrated a small scale AER using natural gas with >95% natural gas conversion, >95% CO conversion to CO₂, and >95% CO₂ capture.
- Demonstrated sorbent durability of over 3,000 hours in CO₂/N₂ thermal (dry) cycling in thermogravimetric analyzer and over 500 cycles of steam reforming/combustion gas regeneration in a 1kW reactor.
- Scaled-up sorbent production process to produce >100 kg batches of sorbent.
- Modeled and optimized the AER process using a dynamic process simulator calibrated with data from 1kW reactors.
- Designed 50 kW stand alone reformer.

Future Directions

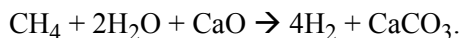
- Produce large scale quantities of sorbent extrudates for 50 kW reformer.
- Build 50 kW reformer.
- Test 50 kW reformer for extended 24/7 operation.
- Continue performance improvement of sorbents and catalysts.

Introduction

Chevron Technology Ventures LLC (CTV) is developing a natural gas fueled 50 kW fuel processor capable of producing a high hydrogen concentration reformat and containing low levels of carbon oxides. This will be done via the AER process using a new catalyst powder manufacturing technique developed by Cabot Superior Micropowders (CSMP). The spray-based powder manufacturing approach allows the creation of materials with unique microstructures and compositions that we believe cannot be achieved by conventional powder manufacturing approaches. The combination of CSMP's unique powder manufacturing capabilities, Chevron's refining catalyst experience, and CTV's natural gas reforming/fuel cell experience presents the opportunity for higher fuel cell power plant efficiencies, reduced capital costs, and long term environmental benefits.

Approach

This project makes use of the fact that the removal of CO₂ during steam reforming of natural gas shifts the equilibrium of both the reforming and water-gas-shift (WGS) reactions to increase the production hydrogen and decrease the production of CO₂ and CO. This enables the production of a high purity hydrogen feed stream based on the overall reaction:



This leads not only to a lower cost, highly efficient fuel processor, but also reduces the cost (higher H₂ content = less precious metal in the membrane electrode assembly) and improves the durability of the fuel cell stack through omission of CO (poison) and CO₂ (reverse WGS and acidity enhancer). We estimate this system will achieve at least 78% energy efficiency, with less than 2 ppm CO, and less than 50 ppb H₂S reformat.

Results

Task 1: Materials Development and Characterization

Based on previous sorbent screening experiences, the evaluation and identification of

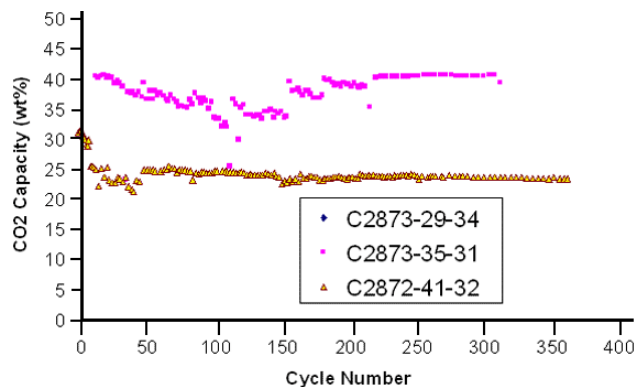


Figure 1. Multi-Cycle CO₂ Trapping Capacity

promising sorbent materials continue to progress. Figure 1 shows that some materials developed thus far can maintain a high CO₂ trapping capacity even after 350 thermal cycles (>3,000 hours) of trapping and releasing CO₂. The work to optimize the synthesis parameters of the promising materials including effects of precursors, type and content of additives and inert materials, and spray conversion conditions continues. The new large-scale spray conversion, powder thermal treatment, extrusion, and pellet-calcination processes at CSMP have been installed and are being optimized both for production rate and performance.

Task 2: Catalyst and CO₂ Absorbent Performance Testing

A series of the identified materials for scale-up have been prepared and tested this year. The sorbent materials tested include the powders optimized under different preparation conditions and the extrudates obtained from the improved recipe and treatment conditions.

The long-term testing of selected absorbent extrudates has continued and the materials have been continuously showing stable CO₂ capacity with minimal performance loss. A comparison of properties for fresh and cycled absorbents such as morphology, porosity and phase composition has been made. Figure 2 is a picture of one of the best extrudates after 500 cycles of testing in a thermogravimetric analyzer (TGA). Through the accelerated CO₂-TGA testing protocol, the materials to meet the requirement of the AER process are further optimized.

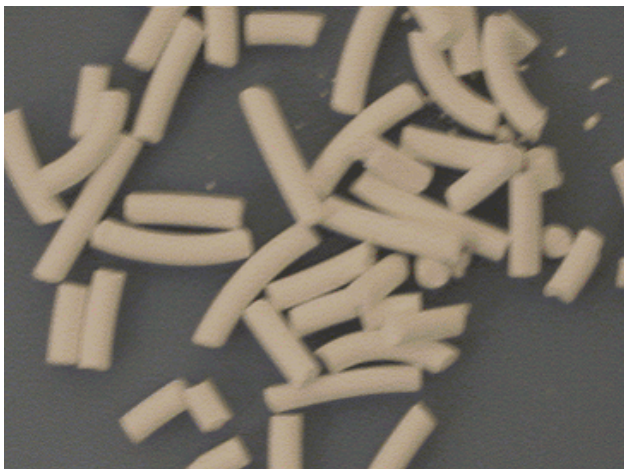


Figure 2. Extrudates after 500 Cycles of Sorption and Regeneration

Task 3: Powder Production Scale Up

As part of the sorbent scale-up production effort at CSMP, a large-scale calciner has been installed and commissioned for the thermal treatment of the sorbent powder, and a large-scale dough mixer was purchased for sorbent extrusion. A crush strength analyzer has been installed at CSMP and the powder extrusion procedure was optimized to maximize product pellet strength. The extrusion and pellet-calcination have been scaled-up an order of magnitude. The sorbent production variation at scale has been statistically quantified and the production operation is being fine tuned from a quality control perspective.

Task 4: Reformer Concept Testing

We have chosen our process design using both data from the 1 kW reactor testing and dynamic modeling using the Aspen custom process simulator with kinetic parameters calibrated to match the 1 kW reactor performance.

Task 5: Reactor Design and Construction

A reactor design very similar to the one used for the 1 kW size reactor has been chosen for the 50 kW reformer. Cost estimates are in preparation.

Task 6: Reactor Testing

The two microreactors in operation are being used to screen and compare sorbent/reforming catalyst combinations.

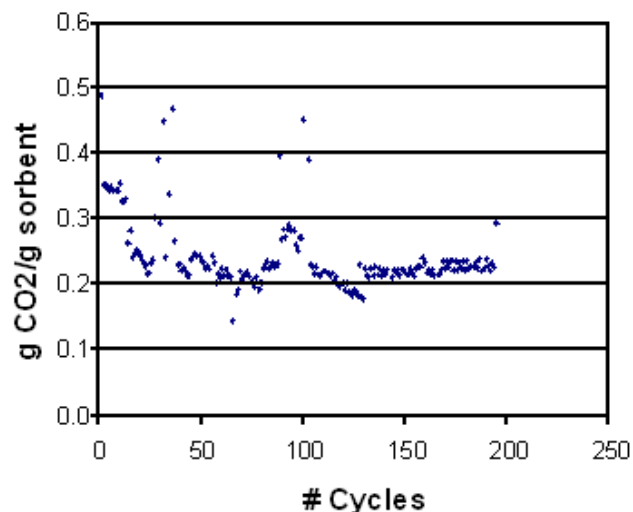


Figure 3. CO₂ Trapping Capacity After Multiple Cycles of Steam Reforming and Regeneration Using Natural Gas Burner Flue Gas

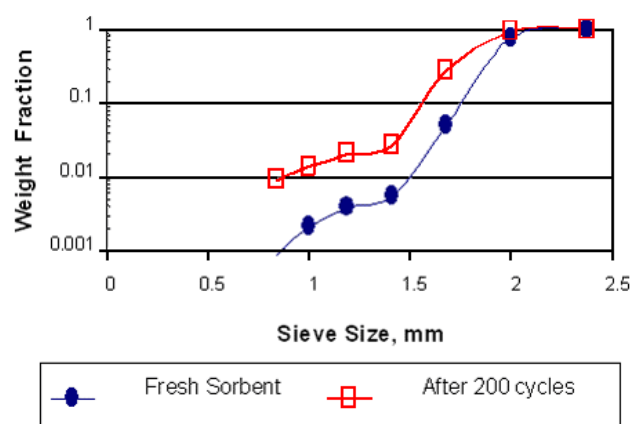


Figure 4. Change in Size Distribution After 200 Cycles of Steam Reforming and Regeneration Using Natural Gas Burner Flue Gas

Both 1kW reactors are operational and are being used to test large batches of sorbents and the effect of process operating parameters such as temperature and steam/carbon ratio on hydrogen production. We have completed tests of more using various regeneration schemes. The effect of many cycles of reforming and regeneration using direct contact from natural gas combustion in a 1kW reactor can be seen in Figure 3. The change in particle size of the sorbent extrudates (durability) over many cycles is shown in Figure 4.

Task 7: 50kW Fuel Processor Construction

The process design for the final fuel processor has been completed. Detailed design, component selection and bidding, and fabricator selection are in progress.

Conclusions

- It is possible to make calcium-based sorbents that maintain a high capacity for CO₂ trapping over many cycles.

- Regeneration of sorbent using direct contact of natural gas combustion products is the preferred method for small batch reactors.
- Absorption-Enhanced Reforming can meet 2005 DOE efficiency and reformat quality targets.

FY 2005 Publications and Presentations

1. “Cost Effective Production of Near Pure Hydrogen”, Fuel Cell and Hydrogen Futures Conference, Perth, Australia, September 2004.